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TRANSMITTAL LETTTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

Attorney Docket No. 01088

U.S. Application No. (if known, see 37 CFR 1.5) 09/807434

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FR99/02652	October 29, 1999	November 5, 1998

TITLE OF INVENTION
METHOD FOR PREPARING ACETIC ACID AND/OR METHYL ACETATE IN THE PRESENCE OF IRIDIUM AND PLATINUM

APPLICANT(S) FOR DO/EO/US
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Applicant herewith submits to the United States Designated Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3).
   a. ☐ are transmitted herewith (only if not required by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5).

Items 11 to 16 below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ As assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:
    Application Data Sheet

	CALCULATIONS	PTO USE ONLY
17. ☒ The following fees are submitted: **BASIC NATIONAL FEE (37 CFR 1.492 (a)(1)-(5):** Neither international preliminary examination fee (37 CFR 1.482) Nor international search fee (37 CFR 1.445(a)(2) paid to USPTO And International Search Report not prepared by EPO or JPO........... $1,000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by EPO or JPO..........$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International search fee (37 CFR 1.445(a)(2)) paid to USPTO........... $710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) But all claims did not satisfy provisions of PCT Article 33(1)-(4)..........$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) And all claims satisfied provisions of PCT Article 33(1)-(4)............... $100.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$860.00	
Surcharge of **$130.00** for furnishing oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e).	$	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	30 -20=	10	X $18.00	$180.00	
Independent Claims	1 -3=		X $80.00	$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				$	
TOTAL OF ABOVE CALCULATIONS =				$1040.00	
Reduction of ½ for filing by small entity, if applicable. A Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				$	
SUBTOTAL =				$1040.00	
Processing fee of **$130.00** for furnishing English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f).				$	
TOTAL NATIONAL FEE =				$1040.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31).				$40.00	
TOTAL FEES ENCLOSED =				$1080.00	
				Amount to be refunded:	$
				charged:	$

a. ☐ A check in the amount of $ to cover the above fees is enclosed.

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d. ☒ A payment of $ 1080.00 is made by credit card. A Credit Card Payment Form (PTO-2038) is attached hereto. The Commissioner is hereby authorized to charge payment of any additional filing fees required under 37 CFR 1.16 or any patent application processing fees under 37 CFR 1.17, or credit any over payment to the credit card account shown on the attached Credit Card Payment Form. Refund of all amounts overpaid, including those of twenty-five dollars or less, is specifically requested. Any fees not accepted by the credit card shown on Form PTO-2038 may be charged to Deposit Account No. 04-0753.

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REGISTRATION NUMBER

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

CAROLE LE BERRE et al **PCT**

Serial No.: none assigned
(PCT/FR99/02652)

Filed: Concurrently Herewith

For: METHOD FOR PREPARING ACETIC ACID AND/OR METHYL ACETATE IN THE PRESENCE OF IRIDIUM AND PLATINUM

PRELIMINARY AMENDMENT AND INFORMATION DISCLOSURE STATEMENT

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

Before calculation of the filing fee, please amend the above-identified application as follows:

IN THE CLAIMS:

Please enter into the application the amendments set forth below and in the attached Appendix:

1.(Amended) A process for the preparation of acetic acid, methyl acetate or both acetic acid and methyl acetate in a liquid phase reaction medium comprising carbonylation of methanol, isomerization of methyl formate or both processes, in the presence of water, a solvent, a homogeneous catalyst

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system comprising iridium and a halogen-containing promoter, and carbon monoxide, wherein said catalyst system also comprises platinum.

2.(Amended) The process as claimed in claim 1 which is a process for the carbonylation of methanol wherein a carbon monoxide partial pressure of between $0.1.10^5$ Pa and 200.10^5 Pa is maintained throughout the process.

3.(Amended) The process as claimed in claim 1 which is a process for the isomerization of methyl formate wherein a carbon monoxide partial pressure of between $0.1.10^5$ Pa and 25.10^5 Pa is maintained throughout the process.

4.(Amended) The process as claimed in claim 1 which comprises a simultaneous methanol carbonylation reaction and a methyl formate isomerization reaction, wherein said process is carried out under a carbon monoxide partial pressure of between $0.1.10^5$ Pa and 25.10^5 Pa throughout the process.

5.(Amended) The process as claimed in claim 1, wherein the platinum is introduced into said catalyst system in the form of metallic platinum, a platinum salt or an oxide.

6.(Amended) The process as claimed in claim 1, wherein the platinum is introduced into the catalyst system in the form of a coordination complex.

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9.(Amended) The process as claimed in claim 6, wherein a platinum content of at least 1 mmol/l of reaction medium and an atomic ratio of iridium to platinum of between 1 and 5 are maintained.

10.(Amended) The process as claimed in claim 1, wherein said catalyst system also contains rhodium.

11.(Amended) The process as claimed in claim 10, wherein rhodium and iridium are maintained in an atomic ratio of rhodium to iridium of between 0.01 and 99.

12.(Amended) The process as claimed in claim 10, wherein the platinum is introduced into the catalyst system in the form of metallic platinum, a platinum salt or a platinum oxide, and a platinum content of at least 4 mmol/l of reaction medium and an atomic ratio of (iridium + rhodium) to platinum of between 2 and 5 are maintained.

13.(Amended) The process as claimed in claim 10, wherein the platinum is introduced in the form of a coordination complex, and a platinum content of at least 1 mmol/l of reaction medium and an atomic ratio of (iridium + rhodium) to platinum of between 1 and 5 are maintained.

14.(Amended) The process as claimed in claim 1, wherein a concentration of iridium in the reaction medium of between 0.1 and 100 mmol/l is maintained.

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15.(Amended) The process as claimed in claim 1 which is carried out in the presence of a water content less than or equal to 14% by weight of the reaction medium.

16.(Amended) The process as claimed in claim 15 wherein only the carbonylation of methanol is carried out and the reaction medium contains water in an amount of between 2 and 8% by weight.

17.(Amended) The process as claimed in claim 15 which comprises a methyl formate isomerization reaction and optionally, a simultaneous methanol carbonylation reaction and the reaction medium contains water in an amount of less than 5% by weight.

18.(Amended) The process as claimed in claim 1, wherein said halogen-containing promoter comprises an elemental halogen or a halogen in a compound with hydrogen or a methyl or acetyl radical.

20.(Amended) The process as claimed in claim 1 which is carried out in the presence of a halogen-containing promoter in an amount of less than or equal to 20% by weight of the reaction medium.

21.(Amended) The process as claimed in claim 1 which is carried out in the presence of an ester in an amount of less than 40% by weight of the reaction medium.

22.(Amended) The process as claimed in claim 1, wherein iodides are introduced into the reaction medium in an amount sufficient to maintain an atomic ratio of soluble iodides introduced into the reaction medium to iridium of less than 10.

23.(Amended) The process as claimed in any claim 1 which is carried out continuously.

--24.(New) The process as claimed in claim 6, wherein the coordination complex is a coordination complex of platinum with at least one ligand selected from the group consisting of carbon monoxide, a carbon monoxide/halogen combination, organonitrogen compounds and organophosphorus compounds.

25.(New) The process as claimed in claim 10, wherein a concentration of iridium and rhodium in the reaction medium of between 0.1 and 100 mmol/l is maintained.

26.(New) The process as claimed in claim 14, wherein a concentration of iridium in the reaction medium of between 1 and 20 mmol/l, is maintained.

27.(New) The process as claimed in claim 15 which is carried out in the presence of a water content less than or equal to 10% by weight of the reaction medium.

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28. (New) The process as claimed in claim 17, wherein the reaction medium contains water in an amount of less than 2% by weight.

29. (New) The process as claimed in claim 20 which is carried out in the presence of a halogen-containing promoter in an amount of less than or equal to 15% by weight of the reaction medium.

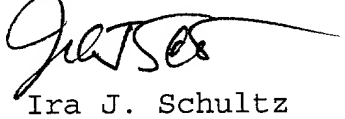
30. (New) The process as claimed in claim 21 which is carried out in the presence of an ester in an amount of less than 30% by weight of the reaction mixture.--

REMARKS

The claims have been amended to delete all multiple dependencies and to generally place the claims in proper form for U.S. practice.

Submitted herewith is the Search Report of the corresponding International application, together with copies of the references cited therein, which are listed on the attached Form PTO-1449.

Respectfully submitted,



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APPENDIX

1.(Amended) A process for the preparation of acetic acid, [and/or] methyl acetate or both acetic acid and methyl acetate in [the] a liquid phase reaction medium [by the] comprising carbonylation of methanol, [and/or the] isomerization of methyl formate or both processes, in the presence of water, a solvent, a homogeneous catalyst system comprising iridium and a halogen-containing promoter, and carbon monoxide, wherein said catalyst system also comprises platinum.

2.(Amended) The process as claimed in claim 1 which is a process for the carbonylation of methanol wherein a carbon monoxide partial pressure of between $0.1.10^5$ Pa and 200.10^5 Pa is maintained throughout the [reaction] process.

3.(Amended) The process as claimed in claim 1 which is a process for the isomerization of methyl formate wherein a carbon monoxide partial pressure of between $0.1.10^5$ Pa and 25.10^5 Pa is maintained throughout the [reaction] process.

4.(Amended) The process as claimed in claim 1 which comprises a simultaneous methanol carbonylation reaction and a methyl formate isomerization reaction, [simultaneously and] wherein said process is carried out under a carbon monoxide

partial pressure of between 0.1.10^5 Pa and 25.10^5 Pa throughout the [reaction] process.

5.(Amended) The process as claimed in [one of claims 1 to 4] claim 1, wherein the platinum is introduced into said catalyst system in the form of metallic platinum [in the metallic state], a platinum salt or an oxide.

6.(Amended) The process as claimed in [one of claims 1 to 4] claim 1, wherein the platinum is introduced into the catalyst system in the form of a coordination complex[, preferably a coordination complex of this metal with ligands selected from carbon monoxide, a carbon monoxide/halogen combination and organonitrogen and organophosphorus compounds].

9.(Amended) The process as claimed in claim 6, [or 7] wherein a platinum content of at least 1 mmol/l of reaction medium and an atomic ratio of iridium to platinum of between 1 and 5 are maintained.

10.(Amended) The process as claimed in [one of claims 1 to 7] claim 1, wherein said catalyst system also contains rhodium.

11.(Amended) The process as claimed in claim 10, wherein [the atomic ratio of] rhodium [to] and iridium [is]

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are maintained in an atomic ratio of rhodium to iridium of between 0.01 and 99.

12.(Amended) The process as claimed in claim 10, [or 11] wherein the platinum is introduced into the catalyst system in the form of metallic platinum [in the metallic state], a platinum salt or a platinum oxide, and a platinum content of at least 4 mmol/l of reaction medium and an atomic ratio of (iridium + rhodium) to platinum of between 2 and 5 are maintained.

13.(Amended) The process as claimed in claim 10, [or 11] wherein the platinum is introduced in the form of a coordination complex [as defined in one of claims 6 or 7], and a platinum content of at least 1 mmol/l of reaction medium and an atomic ratio of (iridium + rhodium) to platinum of between 1 and 5 are maintained.

14.(Amended) The process as claimed in [one of claims 1 to 13] claim 1, wherein a concentration of iridium [and, if appropriate, iridium and rhodium] in the reaction medium of between 0.1 and 100 mmol/l[, preferably of between 1 and 20 mmol/l,] is [used] maintained.

15.(Amended) The process as claimed in [one of claims 1 to 14] claim 1 which is carried out in the presence of a water content less than or equal to 14% by weight[, based

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on the total weight] of the reaction medium[, and preferably a content less than or equal to 10% by weight].

16.(Amended) The process as claimed in claim 15 wherein only the carbonylation of methanol is carried out and [this is done in the presence of a water content of] the reaction medium contains water in an amount of between 2 and 8% by weight [of the reaction medium].

17.(Amended) The process as claimed in claim 15 which [involves] comprises a methyl formate isomerization reaction and[, if appropriate] optionally, a simultaneous methanol carbonylation reaction and [this is carried out in the presence of a water content of] the reaction medium contains water in an amount of less than 5% [and preferably of less than 2%] by weight [of the reaction medium].

18.(Amended) The process as claimed in [one of claims 1 to 17] claim 1, wherein said halogen-containing promoter [can be the] comprises an elemental halogen [by itself] or [can comprise] a halogen in a compound with hydrogen or a methyl or acetyl radical.

20.(Amended) The process as claimed in [one of claims 1 to 19] claim 1 which is carried out in the presence of a [content of] halogen-containing promoter in an amount of less than or equal to 20% by weight[, based on the total

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weight] of the reaction [mixture, and preferably less than 15%] medium.

21. (Amended) The process as claimed in [one of claims 1 to 20] claim 1 which is carried out in the presence of an ester [content] in an amount of less than 40% by weight[, based on the total weight] of the reaction medium [mixture, and preferably of less than 30%].

22. (Amended) The process as claimed in [one of claims 1 to 21] claim 1, wherein iodides are introduced into the reaction medium in [proportions such that the] an amount sufficient to maintain an atomic ratio of soluble iodides introduced into the reaction medium to iridium [is kept below] of less than 10.

23. (Amended) The process as claimed in any [one of claims 1 to 22] claim 1 which is carried out continuously.

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Method for preparing acetic acid and/or methyl acetate in the presence of iridium and platinum

The present invention relates to a process for the preparation of acetic acid and/or methyl acetate in the liquid phase in the presence of a homogeneous catalyst comprising iridium and platinum.

The process of the invention makes it possible to obtain an increased productivity in terms of acetic acid, as well as an improved stability of the catalyst system employed.

Various ways of obtaining acetic acid are known and exploited in industry. These include the methanol carbonylation reaction carried out in the liquid phase, under a pressure of carbon monoxide, which is one of the reactants, in the presence of a homogeneous catalyst system. Another way of obtaining acetic acid consists in isomerizing methyl formate. This reaction, too, is generally carried out in the presence of a catalyst system in the homogeneous phase. Finally, another process involves carrying out the carbonylation of methanol and the isomerization of methyl formate simultaneously.

More precisely, the carbonylation process using rhodium is a known process, exploited in industry, which has formed the subject of numerous articles and patents, for example American patents US 3,769,329 and US 3,813,428.

European patents EP 618 183 and EP 618 184, and European patents EP 785 919 and EP 759 022, describe a carbonylation process carried out in the presence of a catalyst system based on iridium and, if appropriate, also containing rhodium.

A carbonylation process using iridium and ruthenium, which is currently exploited in industry, is described in European patent EP 643 034.

More recently, a new preparative process, consisting of a methyl formate isomerization reaction in the presence of iridium, was proposed in French patent FR 2 746 794 and international patent application WO 97/35829.

In parallel, a process for the preparation of acetic acid and/or methyl acetate by carrying out a methyl formate isomerization reaction and a methanol carbonylation reaction simultaneously was proposed in patent FR 2 746 795 and international patent application WO 97/35828.

These different processes for acetic acid production are generally carried out continuously in plants comprising essentially three zones. The first corresponds to the actual reaction zone comprising a pressurized reactor in which the carbonylation

and/or isomerization are carried out. The second consists of a zone for separation of the acid formed. This operation is effected by partial vaporization of the reaction mixture in a so-called flash apparatus, in which the pressure is kept below that in the reactor. The vaporized part is then sent to a third zone, where the acetic acid produced is purified. This zone comprises various distillation columns in which the acetic acid produced is separated from the water, the reactants and the by-products. That part of the mixture which remains in liquid form at the outlet of the vaporization zone, and comprises especially the catalyst, is recycled to the reactor.

The aim of the process according to the invention is to improve the processes described above by using a homogenous phase catalyst system comprising iridium and platinum.

In fact, it has now been found that the addition of platinum to a catalyst system based on iridium or iridium and rhodium makes it possible, totally unexpectedly, to increase the acid production rate. In other words, the process according to the invention makes it possible to achieve a reaction rate which is greater than or equal to that obtained, under the same conditions, with a catalyst system involving only iridium or an iridium/rhodium mixture, while the total number of moles of metals used in the process of the invention remains unchanged.

Apart from the productivity increase, obtaining comparable rates using a smaller number of moles of catalyst constitutes an additional economic advantage, namely that of reducing the catalyst costs.

It has also been shown that platinum considerably enhances the stability of the iridium, even when the water content is low.

The process according to the invention is carried out in the liquid phase. Consequently the catalyst system used is in a form soluble in the reaction medium.

The catalyst system suitable for carrying out the invention is based on at least one iridium compound, by itself or in the presence of rhodium, and at least one halogen-containing promoter and also comprises at least one platinum derivative.

Thus, according to one of its essential characteristics, the invention relates to a process for the preparation of acetic acid and/or methyl acetate in the liquid phase by the carbonylation of methanol and/or the isomerization of methyl formate in the presence of water, a solvent, a homogeneous catalyst system comprising iridium and a halogen-containing promoter, and carbon monoxide, wherein said catalyst system also comprises platinum.

The invention therefore consists in improving the processes for the

preparation of acetic acid by isomerization, by carbonylation or by a combination of isomerization and carbonylation by using a catalyst system based on soluble iridium and a halogen-containing promoter, and by adding platinum to said catalyst system in a form soluble in the medium.

In a first variant of the process of the invention, methanol is carbonylated by maintaining a carbon monoxide partial pressure of between $0.1.10^5$ Pa and 200.10^5 Pa throughout the reaction.

In a second variant of the process, methyl formate is isomerized by maintaining a carbon monoxide partial pressure of between $0.1.10^5$ Pa and 25.10^5 Pa throughout the reaction. The preferred conditions for carrying out such a process can be obtained directly by those skilled in the art by reference to international patent application WO 97/35829 cited above, except that platinum is added to the iridium.

In a third variant of the process, a methanol carbonylation reaction and a methyl formate isomerization reaction are carried out simultaneously by maintaining a carbon monoxide partial pressure of between $0.1.10^5$ Pa and 25.10^5 Pa throughout the reaction. The preferred conditions for carrying out such a process can be obtained directly by those skilled in the art by reference to international patent application WO 97/35828 cited above, except that platinum is added to the iridium.

In the catalyst system used in the above three variants, the iridium may advantageously be replaced with a combination of iridium + rhodium.

In cases where a catalyst system containing rhodium is employed, the atomic ratio of rhodium to iridium may vary within wide limits, i.e. between 0.01 and 99.

In all these variants, the platinum will be introduced into the reaction medium in a sufficient amount and in appropriate proportions relative to the iridium. Experiments carried out by the inventors of the present invention have in fact shown that the optimum amounts and proportions of platinum are intimately associated with the form in which the platinum is introduced into the reaction medium.

In precise terms, it is possible to use any platinum compounds which are soluble or capable of being solubilized in the reaction medium under the conditions of the invention.

As examples, and without implying a limitation, the following are particularly suitable for carrying out the invention:

- platinum compounds hereafter referred to as "simple compounds", such as platinum in the metallic state, its salts and its oxides; and

- coordination complexes of this metal.

The compounds in the form of complexes prove to be the preferred compounds according to the invention.

The salts used are preferably platinum halides. The halogen is more particularly selected from chlorine, bromine and iodine, the last of these being preferred.

Thus compounds such as PtI_2, $PtBr_2$, $PtCl_2$, $PtCl_4.xH_2O$, $H_2PtCl_6.xH_2O$, $Na_2PtCl_4.xH_2O$ and $Na_2PtCl_6.xH_2O$ can be used in the process according to the invention.

Oxides, selected from PtO, PtO_2 and $PtO_2.xH_2O$, can likewise be appropriately used in the process according to the invention.

As far as the soluble platinum coordination complexes are concerned, the most commonly used compounds are those having ligands selected from carbon monoxide and a carbon monoxide/halogen combination, the halogen being selected from chlorine, bromine and, more particularly, iodine. It is not excluded, however, to use soluble platinum complexes whose ligands are selected for example from organophosphorus and organonitrogen compounds.

The following compounds may be mentioned, without implying a limitation, as coordination complexes which are known to those skilled in the art and are particularly suitable for carrying out the invention: $PtI_2(CO)_2$, $[PtI_2(CO)]_2$, $[Pt_3(CO)_6]^{2-}[Q^+]_2$ and $[Pt_6(CO)_{12}]^{2-}[Q^+]_2$, in which formulae Q can be especially hydrogen or a group NR_4 or PR_4, where R is selected from hydrogen and/or a hydrocarbon radical, tetraiododicarbonyldiplatinum, $[PtI_2(CO)]_2$, being preferred.

In a first variant of the invention, if the platinum is introduced in the form of a simple compound - platinum in the metallic state, salts or oxides - it will be preferable to maintain a platinum content of at least 4 mmol/l of reaction medium and an atomic ratio of iridium to platinum of between 2 and 5.

In a second, particularly preferred variant of the invention, if the platinum is introduced in the form of a coordination complex of this metal with ligands selected from carbon monoxide, a carbon monoxide/halogen combination and organo-nitrogen and organophosphorus compounds, it will be preferable to maintain a platinum content of at least 1 mmol/l of reaction medium and an atomic ratio of iridium to platinum of between 1 and 5.

The atomic ratio of iridium to platinum or, in the case where the catalyst system also comprises rhodium, the atomic ratio of (iridium + rhodium) to platinum

is between 2 and 5 when the platinum is used in the form of simple compounds as defined above, and between 1 and 5 when the platinum is introduced in the form of coordination complexes. The platinum content will preferably be at least 4 mmol/l of reaction medium in the case of simple platinum compounds and at least about 1 mmol/l in the case of coordination complexes.

In general, the concentration of iridium or, if appropriate, iridium + rhodium in the reaction medium is between 0.1 and 100 mmol/l, preferably between 1 and 20 mmol/l.

Any of the rhodium- and iridium-based compounds conventionally used in carbonylation and/or isomerization reactions can be employed in the process according to the invention.

It is possible to use any iridium compounds which are soluble or capable of being solubilized in the reaction medium under the operating conditions of the invention. As examples, and without implying a limitation, iridium in the metallic state, salts of this metal, oxides or coordination complexes are particularly suitable for carrying out the invention.

The iridium salts conventionally used are iridium halides. The halogen is more particularly selected from chlorine, bromine and iodine, the last of these being preferred. Thus compounds like IrI_3, $IrBr_3$, $IrCl_3$, $IrI_3.4H_2O$, IrI_4 and $IrBr_3.4H_2O$ can be used in the process according to the invention.

Oxides, selected from IrO_2 and $Ir_2O_3.xH_2O$, can likewise be appropriately used in the process according to the invention.

As far as soluble iridium coordination complexes are concerned, the most commonly used compounds are those having ligands selected from carbon monoxide and a carbon monoxide/halogen combination, the halogen being selected from chlorine, bromine and, more particularly, iodine. It is not excluded, however, to use soluble iridium complexes whose ligands are selected for example from organophosphorus and organonitrogen compounds.

The following compounds may be mentioned, without implying a limitation, as coordination complexes which are known to those skilled in the art and are particularly suitable for carrying out the invention: $Ir_4(CO)_{12}$, $Ir(CO)_2I_2^-Q^+$, $Ir(CO)_2Br_2^-Q^+$ and $Ir(CO)_2Cl_2^-Q^+$, in which formulae Q can be especially hydrogen or a group NR_4 or PR_4, where R is selected from hydrogen and/or a hydrocarbon radical.

These catalysts can be obtained by any method known to those skilled in the

art. Reference may thus be made to patents EP 657 386 and EP 737 103 for the preparation of iridium-based catalyst solutions suitable for carrying out the present invention.

As indicated previously, the reaction according to the invention can be carried out with a catalyst system comprising iridium by itself, or iridium and rhodium, in addition to platinum.

In general, the rhodium- and iridium-based compounds used are selected from coordination complexes of these metals which are soluble in the medium under the reaction conditions. More particularly, the coordination complexes used are those whose ligands are on the one hand carbon monoxide and on the other hand a halogen such as chlorine, bromine or, more particularly, iodine. It is of course possible to use soluble complexes comprising ligands other than those mentioned, such as organophosphorus or organonitrogen ligands in particular. Advantageously, however, the present invention does not require the use of rhodium and iridium complexes of this type.

Thus complexes of the type $Ir_4(CO)_{12}$, $Ir(CO)_2I_2^-Q^+$, $Ir(CO)_2Br_2^-Q^+$, $Rh_4(CO)_{12}$, $Rh(CO)_2I_2^-Q^+$ or $Rh(CO)_2Br_2^-Q^+$, or complexes based on both metals, such as $Rh_3Ir(CO)_{12}$ or $Rh_2Ir_2(CO)_{12}$, in which formulae Q can be especially hydrogen or a group NR_4 or PR_4, where R is selected from hydrogen and/or a hydrocarbon radical, may be mentioned especially as examples of coordination complexes which are used more particularly in the present invention.

Compounds selected from the salts of these elements, such as especially IrI_3, $IrBr_3$, $IrCl_3$, $IrI_3.4H_2O$, $IrBr_3.4H_2O$, RhI_3, $RhBr_3$, $RhCl_3$, $RhI_3.4H_2O$ and $RhBr_3.4H_2O$, or rhodium and iridium in the metallic state, can likewise be used in the process according to the invention.

It should be noted that the above-mentioned list of rhodium- and iridium-based compounds cannot be considered as exhaustive and that reference may be made to patents US 3 769 329 and US 3 772 380, whose teaching is included herewith, for additional examples of compounds of the two metals mentioned above.

In general, the rhodium-, iridium- and platinum-based compounds used are selected from the coordination complexes of these metals which are soluble in the medium under the reaction conditions. More particularly, the coordination complexes used are those whose ligands are on the one hand carbon monoxide and on the other hand a halogen such as chlorine, bromine or, more particularly, iodine.

It is of course possible to use soluble complexes comprising ligands other than those mentioned, such as organophosphorus or organonitrogen ligands in particular. Complexes of two or three of the above metals may also be mentioned; $[PtRh_5(CO)_{15}]^-Q^+$, Q being as defined above, may be mentioned without implying a limitation.

One important characteristic of the invention lies in the fact that the platinum is present in the reaction medium in a sufficient amount and in appropriate proportions relative to the iridium. The platinum concentration is equal to at least 4 mmol/l of reaction medium and, in addition, the atomic ratio of iridium or (iridium + rhodium) to platinum is between 2 and 5 in the case where simple platinum compounds are used. If the platinum is introduced in the form of a coordination complex, the platinum concentration is preferably equal to at least 1 mmol/l of reaction medium and the atomic ratio of iridium to platinum is between 1 and 5. It has in fact been observed, totally unexpectedly, that such conditions allow a considerable increase in the reaction rate. Remarkably, the stability of the catalyst system is also appreciably improved under these conditions.

Apart from the compounds mentioned above, the catalyst system according to the invention comprises a halogen-containing promoter. This can take the form of a halogen by itself or a halogen combined with other moieties such as hydrogen or the methyl or acetyl radical.

The halogen is generally selected from chlorine, bromine and iodine, iodine being preferred.

Iodine, hydriodic acid, methyl iodide and acetyl iodide may be mentioned as halogen compounds which can also be used as promoters.

Methyl iodide will preferably be used as the halogen-containing promoter.

In one variant of the invention, the halogen-containing promoter is partially or totally introduced into the reaction mixture in the form of a precursor. In such a case, said precursor generally takes the form of a compound which is capable of releasing the hydrocarbon radical of the above-mentioned halogen-containing promoter into the reaction medium under the action of a halogen or a hydrohalic acid in particular, the latter compounds being present in the medium or introduced for this purpose.

Compounds selected from methanol, dimethyl ether, methyl acetate and methyl formate, used by themselves or in a mixture, may be mentioned as non-limiting examples of suitable precursors.

The amount of halogen-containing promoter present in the reaction mixture is advantageously less than or equal to 20%, based on the total weight of said mixture. The content of halogen-containing promoter is preferably less than or equal to 15%.

It should be noted that if the above-mentioned promoter is partially or totally introduced in the form of a precursor, the amount of precursor or promoter/ precursor mixture is such as to give an amount equivalent to that mentioned above.

The process of the invention can be carried out by feeding the reactor with methanol as the only reactant in the case of carbonylation only. It can also be carried out by feeding the reactor with methyl formate in the case of an isomerization process, or with methyl formate and methanol in the case of a combined process involving simultaneous isomerization and carbonylation.

The reaction according to the invention is also carried out in the presence of water. The process according to the invention makes it possible to obtain a good productivity with low water contents, without loss of catalyst metal by precipitation.

Thus the process forming the subject of the invention can be carried out over a wide range of water concentrations in the reaction medium, but preferably with a concentration less than or equal to 14%, based on the total weight of said medium. More particularly, the water content of the reaction medium is less than or equal to 10%.

In the first variant of the process, where only the carbonylation of methanol is carried out, the water content is preferably between 2% and 8% by weight of the reaction medium.

In the second variant, where the isomerization of methyl formate is carried out, optionally simultaneously with the carbonylation of methanol, the water content is less than 5% and preferably less than 2% by weight of the reaction medium.

The process according to the invention can be carried out in the presence of iodides in a form soluble in the reaction medium. The iodides can be introduced into the reaction medium as such, but also in the form of compounds capable of forming soluble iodides.

Iodides are understood as meaning ionic species, i.e. excluding covalent iodides (such as the halogen-containing promoter in particular) and hydriodic acid.

Thus the iodides introduced as such into said mixture are selected from inorganic and organic iodides.

Inorganic iodides which may principally be mentioned are the iodides of alkaline earth metals or alkali metals, the latter being preferred. Potassium iodide, lithium iodide and sodium iodide may be mentioned among said alkali metal iodides.

Organic iodides which may be mentioned are organic compounds comprising at least one organophosphorus group and/or at least one organonitrogen group and reacting with iodine-based compounds to give ionic species containing this halogen. Examples which may be mentioned are the compounds of the formula $Q^+.I^-$, in which Q is a group NR_4 or PR_4, where R is selected from hydrogen and/or a hydrocarbon radical.

Examples which may be mentioned of compounds capable of forming iodides soluble in the reaction medium are alkali metal or alkaline earth metal carboxylates and hydroxides, such as lithium acetate, potassium hydroxide and sodium hydroxide in particular.

It should moreover be noted that the iodides may originate in ways other than those indicated above.

These compounds can thus originate from impurities, such as alkali metals or alkaline earth metals, present in the starting materials employed to prepare the catalyst solution.

Likewise the iodides can originate from the corrosion metals appearing during the reaction. It is preferable to keep the concentration threshold of these metals relatively low, of the order of a few hundred parts per million, because they have the effect especially of favoring the water-gas shift reaction and contribute to increasing the atomic ratio of iodides to iridium.

It is possible to introduce a particular amount of iodides into the reaction medium according to the amount of iridium present in the medium. Thus said amount of iodides introduced is such that the atomic ratio of iodides introduced to iridium (expressed in mol/mol) is below 10 and is kept within this range throughout the reaction.

In one preferred embodiment of the invention, the atomic ratio of iodides to iridium is kept below 3. More particularly, this ratio is below 1.5.

It has been found that the addition of such amounts of iodides makes it possible to improve the stability of the catalyst and keep the productivity of the process high.

Consequently the present invention is more particularly intended to be carried out continuously and the stable operating conditions of the process correspond to the composition and proportions indicated.

More particularly, as far as the soluble iodides are concerned, the atomic ratio of soluble iodides to iridium can be maintained by treating a mixture comprising at least the iridium compound with an ion exchange resin and then adding iodides in soluble form in an amount such that said ratio is below 10.

In addition to the compounds and reactants mentioned above, the reaction according to the invention is advantageously carried out in the presence of esters.

The ester used is preferably methyl acetate and/or methyl formate, which are used as such or in a masked form.

In one embodiment of the invention, the ester content is advantageously less than or equal to 40% by weight, based on the weight of the reaction mixture. More particularly, this content remains less than or equal to 30%.

Finally, the reaction is carried out in the presence of a solvent. The solvent used in the process according to the invention is advantageously acetic acid or formic acid. It is of course possible to use other solvents such as, in particular, compounds which are inert towards the reaction mixture and have a boiling point above that of the acid formed.

The reaction is generally carried out at a temperature between 150 and 250°C. More particularly, the reaction temperature is between 175 and 210°C and preferably between 175 and 200°C.

The total pressure under which the reaction is carried out is generally above atmospheric pressure. More particularly, it is advantageously below 200.10^5 Pa and preferably below or equal to 50.10^5 Pa. In the case of a process according to the invention which involves the isomerization of methyl formate, optionally simultaneously with the carbonylation of methanol, the CO partial pressure will advantageously be between $0.1.10^5$ Pa and 25.10^5 Pa, as indicated previously. The pressures are expressed in absolute pascals and are measured hot, i.e. under the temperature conditions of the reaction.

The process according to the invention is preferably carried out in the

presence of a corrosion metal content of less than a few hundred ppm, preferably of less than 200 ppm. The corrosion metals are especially iron, nickel, chromium, molybdenum and zirconium. The corrosion metal content of the reaction mixture is maintained by the methods known to those skilled in the art, for example selective precipitation, liquid-liquid extraction or passage over ion exchange resins.

In general, the process of the invention is advantageously carried out continuously.

The reaction is carried out in equipment which is resistant to the corrosion created by the medium. Thus zirconium or alloys of the Hastelloy® C or B type are particularly suitable for the operating conditions of the reaction.

When the reaction is started, the various components are introduced into an appropriate reactor, which is fitted with stirring means so as to ensure a good homogeneity of the reaction mixture. It should be noted that although the reactor preferably comprises mechanical means for stirring the reaction mixture, it is not excluded to dispense with such means, it being possible for the mixture to be homogenized by the carbon monoxide introduced into the reactor.

It should be noted that the reaction could conveniently be carried out in a reactor of the piston type.

It is of course possible to envisage combining several reactors of the stirred and piston type.

Carbon monoxide can be introduced directly into the reactor where the reaction according to the invention takes place, but it can also be introduced into the recycling zone, which will be described below.

The reaction mixture leaving the reactor is treated in an appropriate manner for separating the products from the reaction mixture comprising especially the catalyst.

For this purpose, and in the case where the reaction is carried out continuously, it is possible for example to employ a conventional technique which consists in expanding the mixture so as to cause a partial vaporization thereof. This operation can be effected using a valve for expanding the mixture, the latter being introduced into a separator (called a flash separator). The operation can take place with or, preferably, without the provision of heat, i.e. under adiabatic conditions.

The non-vaporized part, comprising especially the catalyst which has remained in solution, is advantageously recycled to the reactor, conventionally by means of a pump.

The vaporized part, which comprises the acetic acid and/or the methyl acetate produced, is then sent to a purification zone, which conventionally comprises various distillation columns.

Finally, the process according to the invention can be carried out with the insertion of an additional reactor between the main reactor and the partial vaporization zone, more particularly upstream of the reaction mixture expansion valve; in said additional reactor, the carbon monoxide present in the dissolved and/or entrained state will be wholly or partially consumed.

The preferred conditions for carrying out such a process can be obtained directly by those skilled in the art by reference to patent FR 2 750 984, except that, according to the invention, platinum is added to the iridium.

EXAMPLES

I - EXAMPLES OF THE CARBONYLATION OF MIXTURES OF METHYL ACETATE + METHANOL IN THE PRESENCE OF PLATINUM(II) IODIDE

Comparative Examples A, B, C, D and E and Examples 1 and 2 according to the invention

A series of experiments were carried out which were identical to one another in every respect except for the nature and composition of the catalyst system. The operating conditions of these experiments are described in detail in Comparative Experiment A below and Table no. 1.

The results obtained in the various experiments are collated in Table no. 2 below, which shows:

- in the column headed V_{carb}, the carbonylation rates calculated on the basis of the CO consumption measured in the reactor after a reaction time of 10 minutes (RT = 10), corresponding to the amount of acetic acid formed by carbonylation during this period; V_{carb} is expressed in mol/l.h;
- in the column headed TOF (= Turnover Frequency), the ratio of the rate to the total metal concentration; TOF is expressed in h^{-1}.

Comparative Experiment A: Carbonylation reaction in the presence of iridium by itself

First of all, the catalyst solution is prepared as follows:

The following are introduced into a 100 ml HASTELLOY® B2 autoclave:

- 0.454 g of iridium iodide,
- 10 g of acetic acid,
- 1 g of water.

The autoclave is then placed under a carbon monoxide absolute pressure of 6 bar at room temperature.

The temperature is raised to 190°C.

The preparation of the catalyst solution takes 25 minutes.

The carbonylation reaction is carried out as follows:

Acetic acid, methyl iodide, water, methanol and methyl acetate are injected into the autoclave under CO pressure.

The initial composition of the reaction mixture is as follows (by weight):

water:	6.4%
methyl acetate:	30%
methyl iodide:	10%
methanol:	5.7%
iridium:	1943 ppm
acetic acid:	qsp 100%

The total absolute pressure is kept constant at 30 bar by injecting carbon monoxide.

The temperature is maintained at 190°C ± 0.5°C.

After the reaction, the reaction liquid weighs 72 g.

The carbonylation rate (V_{carb}) is 11 mol/l/h.

TOF is 1030 h^{-1}.

After the reaction, a light metal deposit is observed in the autoclave.

Comparative Experiments B, C, D and E

Experiments no. 1 and 2 according to the invention

These experiments are carried out under the same operating conditions and with the same initial composition of the reaction mixture except for the catalysts, the details of which are given in Table no. 1, the catalysts being introduced in the form of iridium iodide and/or rhodium iodide and/or platinum(II) iodide.

TABLE no. 1

EXPERIMENT	CATALYSTS			Observations at RT = 10 minutes			
	Iridium iodide (g)	Rhodium iodide (g)	Platinum iodide (g)	Total catalyst content mg/kg (ppm)	Platinum concentration (mmol/l)	Weight of reaction liquid (g)	Volume of reaction liquid (ml)
A (Comparative)	0.454	0	0	1943	0.0	72	68
B (Comparative)	0.782	0	0	3243	0.0	74	70
C (Comparative)	0.256	0.473	0	2392	0.0	75	70
D (Comparative)	0	0	0.48	3114	16.2	67	66
E (Comparative)	0	1.2	0	3361	0.0	76	71
1	0.547	0	0.144	3163	4.7	73	68
2	0.454	0	0.096	2487	3.1	73	69

Initial composition: water=6.4%, AcOMe=30%, MeI=10%, MeOH=5.7%, catalysts according to Table, AcOH=qsp 100%, T=190°C, P total=30 bar

TABLE no. 2

EXPERIMENT	Metal deposit in autoclave at RT = 10 minutes	Rh/Ir (mol/mol)	Ir/Pt (mol/mol)	V(carb) at RT = 10 minutes (mol/h.l)	TOF at RT = 10 minutes (h^{-1})
A (Comparative)	Light deposit	0/100 %	100/0 %	11	1030
B (Comparative)	Deposit	0/100 %	100/0 %	18	1010
C (Comparative)	Deposit	70/30 %	100/0 %	17	860
D (Comparative)	Heavy deposit	0/0 %	0/100 %	0	0
E (Comparative)	Heavy deposit	100/0 %	0/0 %	16.5	470
1	No deposit	0/100 %	73/27 %	21	1190
2	Traces of deposit	0/100 %	75/25 %	10	730

As is clearly apparent from Table 2, all the experiments described above demonstrate the following points:

* Platinum by itself, in the form of platinum(II) iodide, PtI_2, has no catalytic action in the carbonylation of methanol (Experiment D).

* When used in a sufficient amount and in appropriate proportions relative to the iridium (Experiment 1), platinum increases the catalytic activity of the iridium in the carbonylation of methanol, compared with rhodium by itself (Experiment E), iridium by itself (Experiments A and B) and iridium + rhodium (Experiment C).

* Experiment 2, which was not carried out under the optimum conditions of the invention (Pt=3,1 mmol/l), nevertheless shows an improvement in the stability of the catalyst.

* The remarkable stability of the catalysts in Experiment no. 1 according to the invention, since no metal deposit of iridium and/or platinum is observed.

Table no. 2 clearly demonstrates the improvement in the carbonylation rate for a sufficient platinum content in the catalyst system and an appropriate atomic ratio of iridium to platinum.

II - EXAMPLES OF THE CARBONYLATION OF METHYL ACETATE IN THE PRESENCE OF TETRAIODODICARBONYLDIPLATINUM, $[PtI_2(CO)]_2$

Experiments 3, 4, 5 and 6 according to the invention
Comparative Experiments F and G

A series of experiments were carried out which were identical to one another in every respect except for the nature and composition of the catalyst system. The operating conditions of these experiments are described in detail in Comparative Experiment G below and Table no. 3.

The results obtained in the various experiments are collated in Table no. 4, which shows:

- in the column headed V_{carb}, the carbonylation rates calculated on the basis of the CO consumption measured in the reactor for given concentrations of methyl acetate - AcOMe - of 20% and 15% by weight in the reaction mixture, corresponding to the amount of acetic acid formed by carbonylation; V_{carb} is expressed in mol/l.h;

- in the column headed TOF (= Turnover Frequency), the ratio of the rate to the total metal concentration; TOF is expressed in h^{-1}.

Comparative Experiment G: Carbonylation reaction in the presence of iridium by itself

First of all, the catalyst solution is prepared as follows:

The following are introduced into a 100 ml HASTELLOY® B2 autoclave:

- 0.4596 g of iridium iodide,
- 10 g of acetic acid,
- 1 g of water.

The autoclave is then placed under a carbon monoxide absolute pressure of 6 bar at room temperature.

The temperature is raised to 190°C.

The preparation of the catalyst solution takes 25 minutes.

The carbonylation reaction is carried out as follows:

Acetic acid, methyl iodide, water and methyl acetate are injected into the autoclave under CO pressure.

The initial composition of the reaction mixture is as follows (by weight):

water:	6.4%
methyl acetate:	30%
methyl iodide:	10%
methanol:	0%
iridium:	2587 ppm
acetic acid:	qsp 100%

The total absolute pressure is kept constant at 30 bar by injecting carbon monoxide.

The temperature is maintained at 190°C ± 0.5°C.

After the reaction, the reaction liquid weighs 52.3 g.

The carbonylation rate (V_{carb}) is 16 mol/l/h and 14 mol/l/h, respectively, for 20% and 15% by weight of AcOMe.

The corresponding values of TOF are 1110 and 970 h^{-1}.

After the reaction, a metal deposit is observed in the autoclave.

Comparative Experiment F

Experiments no. 3, 4, 5 and 6 according to the invention

These experiments are carried out under the same operating conditions and with the same initial composition of the reaction mixture except for the catalysts, the details of which are given in Table no. 3, the catalysts being introduced in the form of iridium iodide and tetraiododicarbonyldiplatinum, $[PtI_2(CO)]_2$.

TABLE no. 3

	CATALYSTS			Observations at RT = 10 minutes			
EXPERIMENT	Iridium iodide (g)	Rhodium iodide (g)	$[PtI_2(CO)]_2$ (g)	Total catalyst content (ppm)	Pt concentration (mmol/l)	Weight of reaction liquid (g)	Volume of reaction liquid (ml)
F (Comparative)	0	0	0.1662	1399	7.6	48.6	46
G (Comparative)	0.4596	0	0	2587	0.0	52.3	49
3	0.3899	0	0.2491	4143	10.9	52.3	48
4	0.4600	0	0.1662	3989	7.3	51.0	48
5	0.5001	0	0.0844	3429	3.6	53.0	49
6	0.2784	0	0.4134	4894	18.1	51.3	48

Initial composition: water=6.4%, AcOMe=30%, MeI=10%, MeOH=0%, catalysts according to Table, AcOH=qsp 100%, T=190°C, P total=30 bar

TABLE no. 4

EXPERIMENT	Metal deposit in autoclave at RT = 10 minutes	Rh/Ir (mol/mol)	Ir/Pt (mol/mol)	$V_{(carb)}$ at 20 % [AcOMe] (mol/h.l)	TOF at 20 % [AcOMe] ($hour^{-1}$)	$V_{(carb)}$ at 15 % [AcOMe] (mol/h.l)	TOF at 15 % [AcOMe] ($hour^{-1}$)
F (Comparative)	Heavy deposit	0/0 %	0/100 %			2.5 (at RT = 10)	330 (at RT = 10)
G (Comparative)	Deposit	0/100 %	100/0 %	16	1110	14	970
3	No deposit	0/100 %	53/47 %	33	1410	24	1030
4	No deposit	0/100 %	67/33 %	35	1600	29.5	1340
5	No deposit	0/100 %	81/19 %	31	1610	24	1250
6	No deposit	0/100 %	33/67 %	24	890	20	740

All the experiments described above demonstrate the following points:

* Platinum by itself, employed in the form of tetraiododicarbonyldiplatinum, $[PtI_2(CO)]_2$, has a valuable catalytic action in terms of TOF (Experiment F = 330 h^{-1}) compared with platinum by itself in non-carbonylated form (Experiment D = 0 h^{-1}).

* When used in association with iridium (Experiments no. 3, 4 and 5 according to the invention) in a sufficient amount and in appropriate proportions relative to the iridium, platinum in the form of tetraiododicarbonyldiplatinum, $[PtI_2(CO)]_2$, increases the activity of the iridium in the carbonylation of methyl acetate, compared with iridium by itself (Comparative Experiment G).

* Experiment 6, which was not carried out under the optimum conditions of the invention (Ir/Pt = 0.5), nevertheless shows an improvement in the stability of the catalyst.

* The remarkable stability of the catalysts in Experiments no. 3, 4 and 5 according to the invention, since no metal deposit of platinum and/or iridium is observed.

Table no. 4 clearly demonstrates the improvement in the carbonylation rate for a sufficient platinum content in the catalyst system and an appropriate atomic ratio of iridium to platinum.

WHAT IS CLAIMED IS:

1. A process for the preparation of acetic acid and/or methyl acetate in the liquid phase by the carbonylation of methanol and/or the isomerization of methyl formate in the presence of water, a solvent, a homogeneous catalyst system comprising iridium and a halogen-containing promoter, and carbon monoxide, wherein said catalyst system also comprises platinum.

2. The process as claimed in claim 1 which is a process for the carbonylation of methanol wherein a carbon monoxide partial pressure of between $0.1.10^5$ Pa and 200.10^5 Pa is maintained throughout the reaction.

3. The process as claimed in claim 1 which is a process for the isomerization of methyl formate wherein a carbon monoxide partial pressure of between $0.1.10^5$ Pa and 25.10^5 Pa is maintained throughout the reaction.

4. The process as claimed in claim 1 which comprises a methanol carbonylation reaction and a methyl formate isomerization reaction simultaneously and is carried out under a carbon monoxide partial pressure of between $0.1.10^5$ Pa and 25.10^5 Pa throughout the reaction.

5. The process as claimed in one of claims 1 to 4 wherein the platinum is introduced into said catalyst system in the form of platinum in the metallic state, a platinum salt or an oxide.

6. The process as claimed in one of claims 1 to 4 wherein the platinum is introduced into the catalyst system in the form of a coordination complex, preferably a coordination complex of this metal with ligands selected from carbon monoxide, a carbon monoxide/halogen combination and organonitrogen and organophosphorus compounds.

7. The process as claimed in claim 6 wherein said complex is $[PtI_2(CO)]_2$.

8. The process as claimed in claim 5 wherein a platinum concentration of at least 4 mmol/l of reaction medium and an atomic ratio of iridium to platinum of between 2 and 5 are maintained.

9. The process as claimed in claim 6 or 7 wherein a platinum content of at least 1 mmol/l of reaction medium and an atomic ratio of iridium to platinum of between 1 and 5 are maintained.

10. The process as claimed in one of claims 1 to 7 wherein said catalyst system also contains rhodium.

11. The process as claimed in claim 10 wherein the atomic ratio of rhodium to

iridium is between 0.01 and 99.

12. The process as claimed in claim 10 or 11 wherein the platinum is introduced into the catalyst system in the form of platinum in the metallic state, a platinum salt or a platinum oxide, and a platinum content of at least 4 mmol/l of reaction medium and an atomic ratio of (iridium + rhodium) to platinum of between 2 and 5 are maintained.

13. The process as claimed in claim 10 or 11 wherein the platinum is introduced in the form of a coordination complex as defined in one of claims 6 or 7, and a platinum content of at least 1 mmol/l of reaction medium and an atomic ratio of (iridium + rhodium) to platinum of between 1 and 5 are maintained.

14. The process as claimed in one of claims 1 to 13 wherein a concentration of iridium and, if appropriate, iridium and rhodium in the reaction medium of between 0.1 and 100 mmol/l, preferably of between 1 and 20 mmol/l, is used.

15. The process as claimed in one of claims 1 to 14 which is carried out in the presence of a water content less than or equal to 14% by weight, based on the total weight of the reaction medium, and preferably a content less than or equal to 10% by weight.

16. The process as claimed in claim 15 wherein only the carbonylation of methanol is carried out and this is done in the presence of a water content of between 2 and 8% by weight of the reaction medium.

17. The process as claimed in claim 15 which involves a methyl formate isomerization reaction and, if appropriate, a simultaneous methanol carbonylation reaction and this is carried out in the presence of a water content of less than 5% and preferably of less than 2% by weight of the reaction medium.

18. The process as claimed in one of claims 1 to 17 wherein said halogen-containing promoter can be the halogen by itself or can comprise hydrogen or a methyl or acetyl radical.

19. The process as claimed in claim 18 wherein said halogen-containing promoter is methyl iodide.

20. The process as claimed in one of claims 1 to 19 which is carried out in the presence of a content of halogen-containing promoter less than or equal to 20% by weight, based on the total weight of the reaction mixture, and preferably less than 15%.

21. The process as claimed in one of claims 1 to 20 which is carried out in the presence of an ester content of less than 40% by weight, based on the total weight

of the reaction mixture, and preferably of less than 30%.

22. The process as claimed in one of claims 1 to 21 wherein iodides are introduced into the reaction medium in proportions such that the atomic ratio of soluble iodides introduced into the reaction medium to iridium is kept below 10.

23. The process as claimed in any one of claims 1 to 22 which is carried out continuously.

ABSTRACT OF THE DISCLOSURE

The invention relates to a process for the preparation of acetic acid and/or methyl acetate in the liquid phase by the carbonylation of methanol and/or the isomerization of methyl formate in the presence of water, a solvent, a homogeneous catalyst system comprising iridium and a halogen-containing promoter, and carbon monoxide, wherein said catalyst system also comprises platinum.

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

Docket No. _____

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Method for preparing acetic acid and/or methyl acetate in the presence of iridium and platinum, the specification of which

(check one) X is described and claimed in PCT International Application PCT/FR99/02652 filed on 10/29/1999 (MM/DD/YYYY) _____ amended on _____ (if applicable) (OR) ____ is described in United States Application Number _____ filed on (MM/DD/YYYY) _____ (OR) _____ is attached hereto.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, any foreign application for patent or inventor's certificate, or any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Claimed? Yes	No
98/13954	France	11/05/1998	X	____
			____	____
			____	____

I hereby claim the benefit under 35 U.S.C. 119(e) of any Unites States Provisional Application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s), or 365(c) of any PCT International application designating the Unites States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Parent Application or PCT Parent	Parent Filing Date	Parent Patent Number

As a named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. §1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

100

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